

A View of Passive Films on Metals as Mixed-Conducting Oxides

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Understanding the mechanism of generation and transport of ionic and electronic defects in passive films on metallic construction materials is of paramount importance to corrosion prevention. We have recently proposed the mixed-conduction model (MCM) [1-3] to describe quantitatively the correlation between the transport properties of passive films, their composition and structure. In the MCM, the passive film is regarded as a mixed-conducting oxide (see Fig. 1). At the metal / film interface, electrochemical oxidation of the metal leads to the generation of positively charged point defects (anion vacancies or cation interstitials). At the film / solution interface, the electrochemical dissolution of the metal leads to the generation of negatively charged defects (cation vacancies).

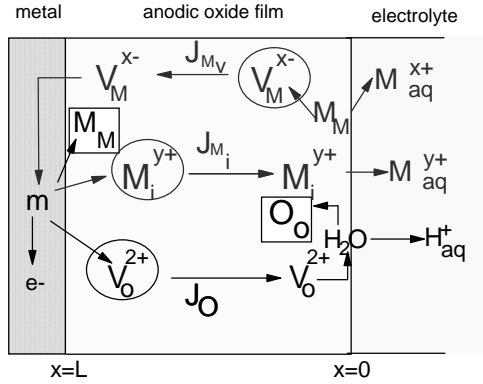


Fig. 1. A scheme of reactions taking place in the passive film.

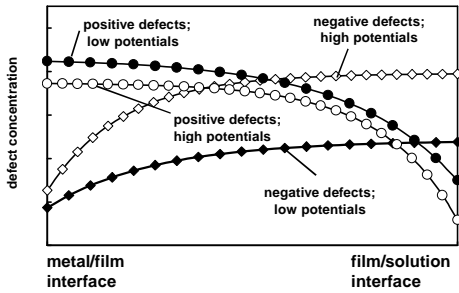


Fig. 2. A sketch of the qualitative shape of the ionic defect profiles in a passive film according to the mixed-conduction model.

The mobilities of ionic point defects in passive films are very low, and as a result a concentration profile of these defects is built up in the steady state (Fig. 2). At low potentials in the passive range, the profile of positive defects predominates and a positive ionic space charge is created close to the metal / film interface. Electroneutrality is maintained by the formation of a negative electronic space charge ensuring the n-type conductivity of the passive film as a whole. At high potentials approaching transpassive dissolution, the profile of negative defects starts to dominate, and a negative space charge is created in the vicinity of the film / solution interface. Electroneutrality is maintained by the formation of a positive electronic space charge leading to a p-type conductivity. Under the assumption that the conductivity of the passive film is predominantly electronic, and ionic transport is governed by high-field migration, equations for the conductivity σ and impedance response Z of the passive film were derived:

$$\sigma = (F^2 D_e / RT) [2 \{ (k_3^0 k_2'^0 / k_1'^0 k_4^0) \exp[(b_3 - b_4)\alpha E] \}^{1/2} \exp(-L/2a) + 1.5k_2'^0 a / D_O' + k_3^0 (a / D_M') \exp(b_3 \alpha E)]$$

$$Z = \{ \{ (a / j\omega \epsilon \epsilon_0) \ln [(1 + j\omega \rho_d \epsilon \epsilon_0 \exp(1/d)) / (1 + j\omega \rho_d \epsilon \epsilon_0)] \}^{-1} + R_{ion}^{-1} \}^{-1}$$

where

$$\rho_d = \{ (F^2 D_e / RT) [(k_3^0 / k_1'^0) \exp(b_3 \alpha E) + (k_2'^0 / k_4^0) \exp(-b_4 \alpha E)] \}^{-1}$$

$$R_{ion}^{-1} = [(2F)^2 / RT] (D_O' / a) (1 - \alpha) (k_2'^0 / k_4^0) \exp(-b_4 \alpha E) \exp(-L/a) + [(3F)^2 / RT] (D_M' / a) (1 - \alpha) (k_3^0 / k_1'^0) \exp(b_3 \alpha E) + [(2F)^2 / RT] (1 - \alpha) k_2'^0,$$

a is the hopping distance, b_i ($i=1-4$) are the Tafel coefficients, C is the space-charge layer capacitance, D_e is the electron (or hole) diffusivity, D_M' and D_O' the apparent (field dependent) diffusivities of cation and anion vacancies, k_i ($i=1-4$) are the interfacial rate constants, k_i^0 are their values at $E=0$, L is film thickness, α is the polarisability of the film /

solution interface, and ϵ is the dielectric constant of the film.

A comparison of these equations with experimental data for passive films formed on Cr, Fe-Cr, Fe-Cr-Mo and Ni-Cr alloys has allowed the determination of the kinetic parameters of defect generation, transport and consumption [1-3].

In the case when the ionic mobility through an anodic film is relatively high, the possibility for mutual compensation of the positive and negative ionic space charges exists. The equation for the impedance response of the system in high-field conditions has been derived in the form [4,5]:

$$Z = V_m \lambda E / j\omega F(1 - \alpha) + \{ j\omega \epsilon \epsilon_0 E / (1 - \alpha) + [i_s (2Fa/RT) E / (1 - \alpha)] [\alpha + (1 - \alpha) i_s S / (j\omega + i_s S)] \}^{-1}$$

where E is the field strength, i_s is the steady-state ionic current density, and S is the cross capture section for ionic defects. A comparison of this equation with experimental data on Al, Nb, Ta, Mo, W, Bi, Fe and Fe-Mo alloys has allowed the determination of the kinetic parameters of the ionic conduction process.

References

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